s9.m1.p9 **Hydrogen Bonds in 13-Hydroxylupanine Epimers.** I. Wolska, T. Borowiak, *Adam Mickiewicz University, Faculty of Chemistry, Department of Crystallography, Grunwaldzka 6, 60-780 Poznan, Poland.*
Keywords: sparteine epimers, unusual conformation.

Lupine alkaloids form a group of chiral bisquinolizidine compounds with a semi-rigid sterostructure. In particular, due to an easy inversion of electronic configuration on N(16) in sparteine skeleton C/D fragment of trans-quino-lizidine system transforms to the cis-one. This gives rise to change of a boat-chair conformation of this fragment into a chair-chair one.

Due to this conformational dynamism the lupine alkaloids, in particular sparteine and its derivatives, are used in organic chiral syntheses, asymmetric catalysis, or as chelating ligands.

Our interests in sparteine conformational flexibility concern the factors affecting conformational transitions. In general, free bases of sparteine and its derivatives possess trans/trans configuration of their both quinolizidine systems A/B and C/D and a boat conformation of their C - ring.

The results presented in this report concern the crystal structures of two epimers of 13-hydroxylupanine: 13α-hydroxylupanine with the axial hydroxy group and 13β-hydroxylupanine with the equatorial one.

The conformation of the ring C is in the both compounds absolutely surprising, as it is a chair form. Both epimers crystallize in the same space group, $P2_12_12_1$, the packing modes are also similar: the both alkaloid molecules are connected in their crystals by intermolecular hydrogen bonds O-H· · · ·O=C into helices along one of the twofold screw axes of symmetry. Probably, the intermolecular hydrogen bonds aforementioned, cause this unusual molecular conformation.

s9.m1.p10 **Neutron diffraction study of very short OHN hydrogen bonds in phenol - pyridine adduct.** I. Majerz[1], T. Steiner[2], S.A. Mason[3], C.C. Wilson[4] *[1] Faculty of Chemistry, University of Wroclaw[2] Institut für Chemie - Kristallographie, Freie Universität, Berlin[3] Institute Laue-Langevin, Grenoble[4] ISIS Rutheford-Appleton Laboratory, Chilton*
Keywords: hydrogen bond, neutron diffraction, phenol-pyridine complex.

Very strong hydrogen bonds play important roles in chemical and enzymatic interactions and are, therefore, subject of great current interest. There are many examples of OHN hydrogen bonds, but most are of relatively moderate strengths. Only in a so-called 'transition region' or 'critical region' characterized by a narrow range of ΔpK_a [$\Delta pK_a = pK_a(NH^+) - pK_a(OH)$] very short and strong OHN bridges can be formed. In these strong hydrogen bonds, the proton may be located closer to the O or closer to the N atom but also in the center of the bridge. The exact position of the proton can only be determined by neutron diffraction.

As part of our systematic studies on pyridine-phenol adducts[1] we have determined three low-T neutron diffraction structures and find the shortest O-H···N and N-H···O hydrogen bonds for which neutron diffraction data are currently available. In 2-methylpyridine-pentachlorophenol (data collection at ISIS, instrument SDX, T = 30 K), the N···O distance is 2.588(3) Å, and the proton is closer to O than to N. In two adducts with the slightly more acidic 2,6-dichloro-4-nitrophenol, the proton is transferred along the bridge, and is found closer to N than to O (data collection at the ILL, instrument D19, T = 15 K). With the acceptor 3-methylpyridine, the O···N distance is 2.538(1) Å, and the distances at the H-atom are H-N = 1.129(2) and H···O = 1.424(2) Å. With the acceptor 3,4-dimethylpyridine, the structure contains two symmetry-independent adducts with significantly different geometries. The results are compared with earlier neutron diffraction studies of OHN hydrogen bonds.

[1] I. Majerz, Z. Malarski, and L. Sobczyk, Proton transfer correlations between the C–O, O–H, N–H and O···N bond lengths in amine phenolates. Chem. Phys. Lett. **274** (1997) 361–364.